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A CONVENIENT AND DIRECT METHOD OF FINDING THE PRINCIPAL IONIC SUSCEPTIBILITIES OF TRICLINIC CRYSTALS

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ABSTRACT. Details of the theory of a general method of finding the three principal ionic susceptibilities of a triclinic crystal have been discussed. The method involves simple magnetic measurements with no approximation or trial and error. Although it is most advantageous and best suited to the case of triclinic crystals, it may as well be applied to other classes of crystals. Ionic anisotropy of a triclinic crystal ($CuSO_4.5H_2O$) and an orthorhombic crystal ($NiSO_4.7H_2O$) have been determined by this method and the results have been compared with those obtained by earlier methods.

INTRODUCTION

Magnetic susceptibility ellipsoid of a crystal is the resultant of the more fundamental magnetic ellipsoids, one belonging to each magnetic complex (a molecule or ionic cluster) in the unit cell, and in general oriented with respect to one another. Theoretical investigations on the nature of the ligand field of the complexes and their magnetic behaviours are directly related with the principal ionic or molecular susceptibility tensors instead of the crystalline values. But the usual method adopted for the determination of the former is first to determine the principal crystalline susceptibilities and then the ionic values with the help of structural angular parameters. The determination of principal crystalline susceptibilities in the case of a triclinic crystal presents many difficulties because of the absence of any symmetry in the crystal. Earlier works (Krishnan and Mookerjee, 1936, 1938; Mathur, 1960) on the measurement of susceptibilities of triclinic crystals consisted of measuring magnetic anisotropies in a large number of non-parallel planes and finding by trial and error method that principal crystalline anisotropies. Evidently the procedure is extremely tedious both experimentally and computationally. A precise and more convenient method recently given by one of us (Ghosh and Bagchi, 1962) although does away with the drawbacks of the earlier methods still involves measurements at least in five different planes and laborious calculations. In addition to these difficulties the determination of the principal ionic values from the crystalline values very often involves

large computational errors depending upon the actual angular relationship between the two sets of tensors.

Since all that is needed for theoretical purposes are the ionic tensors, our aim in the present paper is to give a method by which the principal ionic susceptibility values can directly and easily be found out without determining the principal crystalline susceptibilities. It will be shown that the determination of susceptibilities along any two convenient mutually perpendicular directions in only two planes and the mean susceptibility will suffice to give the three principal ionic susceptibilities from three linear equations provided the angular orientation of each ion is known from other measurements, such as X-ray or paramagnetic resonance studies. It will be also shown that the method becomes more simplified if we consider a uniaxial symmetry of the ion in which case magnetic measurement in one plane only together with the mean susceptibility and one angular parameter for each inequivalent ion will be sufficient to determine the ionic values. Moreover, suitably chosen planes will not only simplify the calculations but also minimise the effect of the errors in the angular parameter data, if any.

THEORY OF THE METHOD

Let us take any one of the three principal crystallographic axes as x-axis, the perpendicular to this lying in the same crystallographic plane as y-axis and line perpendicular to both as z-axis. The direction cosines of the principal susceptibility axes of an ion with respect to x, y and z axes are written in the usual matrix form :

	x	y	z
K_1	α_1	β_1	γ_1
K_2	α_2	β_2	γ_2
K_3	α_3	β_3	γ_3

To generalise the theory we consider more than one ion in the unit cell. In the most general case (Triclinic crystal), these ions may not be related amongst themselves by any symmetry operation (except in the special case of inversion) and hence the direction cosines of the principal ionic susceptibility axes will in general be different for different ions, the three principal values being assumed to be the same for all ions.

The crystalline susceptibility can be described by an ellipsoid whose equation in the x, y, z system is given by

$$\chi_{11}x^2+\chi_{22}y^2+\chi_{33}z^2+2\chi_{12}xy+2\chi_{13}xz+2\chi_{23}yz = 1 \qquad \ldots (1)$$

where,

$$\chi_{11} = \frac{1}{n}\Sigma(K_1\alpha_1{}^2+K_2\alpha_2{}^2+K_3\alpha_3{}^2)$$

$$\chi_{22} = \frac{1}{n}\Sigma(K_1\beta_1^2+K_2\beta_2^2+K_3\beta_3^2)$$

$$\chi_{33} = \frac{1}{n}\Sigma(K_1\gamma_1^2+K_2\gamma_2^2+K_3\gamma_3^2)$$

$$\chi_{12} = \frac{1}{n}\Sigma(K_1\alpha_1\beta_1+K_2\alpha_2\beta_2+K_3\alpha_3\beta_3)$$

$$\chi_{13} = \frac{1}{n}\Sigma(K_1\alpha_1\gamma_1+K_2\alpha_2\gamma_2+K_3\alpha_3\gamma_3)$$

$$\chi_{23} = \frac{1}{n}\Sigma(K_1\beta_1\gamma_1+K_2\beta_2\gamma_2+K_3\beta_3\gamma_3)$$

the summation being taken over all the n ions in the unit cell whose principal susceptibilities are the same but with different orientations in general.

Consider any crystallographic plane whose Millerian indices are (khl) and which is our working plane for magnetic measurement. The direction-cosines (ξ, η, ζ) of the normal to this plane relative to x, y and z axes can be expressed in terms of known crystallographic data as will be done in course of the following discussions. Let the length of the normal to this plane drawn from the origin upto the surface of the ellipsoid be r_N. Taking any two mutually perpendicular semidiameters r_θ and $r_{90+\theta}$ of the ellipsoid in this working plane, r_N r_θ and $r_{90+\theta}$ form an orthogonal set and it can be shown that

$$\frac{1}{r^2_N}+\frac{1}{r_\theta^2}+\frac{1}{r^2_{90+\theta}} = \chi_{11}+\chi_{22}+\chi_{33}$$

i.e.,
$$\chi_{\xi,\eta,\varsigma},+\chi_\theta+\chi_{90+\theta} = \chi_{11}+\chi_{22}+\chi_{33}$$

where $\chi_{\xi,\eta,\varsigma}$, χ_θ and $\chi_{90+\theta}$ are the crystalline susceptibilities along r_N, r_θ and $r_{90+\theta}$ respectively. Hence,

$$\chi_\theta+\chi_{90+\theta} = \chi_{11}+\chi_{22}+\chi_{33}-[\chi_{11}\xi^2+\chi_{22}\eta^2+\chi_{33}\zeta^2+2\chi_{12}\xi\eta+2\chi_{13}\xi\eta+2\chi_{23}\eta\zeta]$$

$$=K_1\Big[1-\frac{1}{n}\Sigma\{(\alpha_1^2\xi^2+\beta_1^2\eta^2+\gamma_1^2\zeta^2)+2(\alpha_1\beta_1\xi\eta+\alpha_1\gamma_1\xi\zeta+\beta_1\gamma_1\eta\zeta)\}\Big]$$

$$+K_2\Big[1-\frac{1}{n}\Sigma\{(\alpha_2^2\xi^2+\beta_2^2\eta^2+\gamma_2^2\zeta^2)+2(\alpha_2\beta_2\xi\eta+\alpha_2\gamma_2\xi\zeta+\beta_2\gamma_2\eta\zeta)\}\Big]$$

$$+K_3\Big[1-\frac{1}{n}\Sigma\{(\alpha_3^2\xi^2+\beta_3^2\zeta^2+\gamma_3^2\zeta^2)+2(\alpha_3\beta_3\xi\eta+\alpha_3\gamma_3\xi\zeta+\beta_3\gamma_3\eta\zeta)\}\Big] \quad (2)$$

Also we have for the mean susceptibility

$$\bar{\chi} = \frac{K_1+K_2+K_3}{3} \quad \ldots (3)$$

Thus measuring $\bar{\chi}$ and $\chi_\theta+\chi_{90+\theta}$ in two planes we get three linear equations from (2) and (3) which on solving gives the principal ionic values, K_1, K_2 and K_3 provided the angul parameters α_i's, β_i's and γ_i's are known. It should be noted that from x-ray structural analysis angles are generally expressed with respect to the principal crystallographic axes with the help of standard mathematical formulae involving the crystallographic angles α, β, γ and co-ordinates of the ligands and as such appropriate transformation is needed to convert them to our co-ordinate system. As a special case, it will be shown that such a transformation is not necessary if a uniaxial symmetry of the ion is considered and the measurement is made in the appropriate plane.

If we take x-axis to be the c-axis of triclinic crystal and y axis in the $a-c$ plane, the expressions for ξ, η, ζ are given by

$$\left.\begin{aligned}
\xi &= \frac{l}{c} \cdot Q \\
\eta &= \left[\frac{h}{a\sin\beta} - \frac{l}{c\tan\beta}\right] Q \\
\zeta &= \left[\left(\frac{k}{b\sin\alpha} - \frac{l}{c\tan\alpha}\right)\frac{1}{\sin\gamma'} - \left(\frac{h}{a\sin\beta} - \frac{l}{c\tan\beta}\right)\frac{1}{\tan\gamma'}\right] Q
\end{aligned}\right\} \quad \ldots (4)$$

where $\gamma' = \cos^{-1}\dfrac{\cos\gamma - \cos\alpha\cos\beta}{\sin\alpha \,.\, \sin\beta}$ is the dihedral angle between $a-c(010)$ and $b-c(100)$ planes given directly from crystallographic data, and

$$Q = \left[\frac{l^2}{c^2} + \left\{\frac{h}{a\sin\beta} - \frac{l}{c\tan\beta}\right\}^2 + \left\{\left(\frac{k}{b\sin\alpha} - \frac{1}{c\tan\alpha}\right)\frac{1}{\sin\gamma'} - \left(\frac{h}{a\sin\beta} - \frac{l}{c\tan\beta}\right)\frac{1}{\tan\gamma'}\right\}^2\right]^{-\frac{1}{2}}$$

and $a : b : c$ is the axial length ratio; α, β, γ are the triclinic angles; h, k, l are the Millerian indices of the (ξ, η, ζ) plane. If the angles of an ionic axis K_i with respect to crystallographic a, b and c axes be quoted in x--ray results as $\phi_i{}^a$, $\phi_i{}^b$ and $\phi_i{}^c$ respectively then the direction cosines α_i, β_i and γ_i with respect to our x, y, z system are given by

$$\left.\begin{aligned}
\alpha_i &= \cos\phi_i{}^c \\
\beta_i &= (\cos\phi_i{}^a - \cos\phi_i{}^c \,.\, \cos\beta)\frac{1}{\sin\beta} \\
\gamma_i &= \pm\sqrt{1-(\alpha_i{}^2+\beta_i{}^2)}
\end{aligned}\right\} \quad \ldots (5)$$

The ambiguity of the sign of γ_i can be removed by finding α_i's, β_i's and γ_i's for all the three K_i's and utilising their orthogonal properties. Instead of taking measure-

ments in two general planes in case of which complicated expressions (2) and (4) are to be used, we can measure $\chi_\theta+\chi_{90+\theta}$ in the horizontal plane with c-axis vertical and $a-c$ plane horizontal.

With c axis vertical, $\xi = 1$, $\eta = \zeta = 0$ and the equation (2) reduces to

$$\chi_\theta+\chi_{90+\theta} = K_1\left[1-\frac{1}{n}\Sigma\alpha_1^2\right]+K_2\left[1-\frac{1}{n}\Sigma\alpha_2^2\right]+K_3\left[1-\frac{1}{n}\Sigma\alpha_3^2\right] \quad \ldots (6)$$

With $a-c$ plane horizontal, $\zeta = 1$, $\xi = \eta = 0$ and we have

$$\chi_\theta+\chi_{90+\theta} = K_1\left[1-\frac{1}{n}\Sigma\gamma_1^2\right]+K_2\left[1-\frac{1}{n}\Sigma\gamma_2^2\right]+K_3\left[1-\frac{1}{n}\Sigma\gamma_3^2\right] \quad \ldots (7)$$

Thus knowing structural angular parameters from X-ray, K_1, K_2 and K_3 can be easily solved from the simple equations (6), (7), (3) and (5).

The above expressions are further simplified if we consider a uniaxial symmetry of the ion i.e. $K_1 = K_2 = K_\perp$ and $K_3 = K_\parallel$. With c-axis vertical magnetic measurement in the horizontal plane gives

$$\chi_\theta+\chi_{90+\theta} = K_\perp\left[2-\frac{1}{n}\Sigma(1-\alpha_3^2)\right]+K_\parallel\left[1-\frac{1}{n}\Sigma\alpha_3^2\right]$$

$$= K_\parallel\left(1-\frac{1}{n}\Sigma\alpha_3^2\right)+K_\perp\left(1+\frac{1}{n}\Sigma\alpha_3^2\right) \quad \ldots (8)$$

and $$\bar{\chi} = (2K_\perp+K_\parallel)/3 \quad \ldots (9)$$

Thus measurement in only one plane and mean susceptibility will give the values of $K_\parallel$ and $K_\perp$ if the angles α_3's are known, for which no transformation of X-ray data is needed according to (5).

EXPERIMENTAL RESULTS

(a) *The case of a triclinic crystal* :

The X-ray structural analysis of Beevers and Lipson (1934) shows that in the unit cell of $CuSO_4 \cdot 5H_2O$ (triclinic class) there are two magnetically inequivalent* ions which are tetragonally distorted. The direction cosines of the

* Ions having parallel or antiparallel orientation with respect to one another will be called magnetically equivalent, since the magnetic ellipsoids for such ions coincide with one another. Ions which are differently oriented with respect to one another will be called magnetically inequivalent although they may be crystallographically equivalent. This terminology appears to have arisen from the needs of description in paramagnetic resonance (Bleaney *et al.*, 1949 and all later works) where such ions give in general different lines. From the point of view of susceptibility such ions behave identically. From this later point, only ions which are crystallographically inequivalent contribute differently to the crystalline tensors.

tetragonal axes (T_1, T_2) of the two ions relative to crystallographic axes are given below. The tetragonal axis has been taken along the normal to the plane containing the square of water oxygens around the central copper.

	a	b	c
T_1	·06075	−·65412	·65236
T_2	·38724	·74786	·40182

Here $n = 2$ and the expression (8) becomes

$$\chi_\theta + \chi_{90+\theta} = K_{\|}[1 - \tfrac{1}{2}(\alpha_3^2 + \alpha'^2_3)] + K_\perp[1 + \tfrac{1}{2}(\alpha_3^2 + \alpha'^2_3)] \quad \ldots \quad (10)$$

$$\bar{\chi} = (K_{\|} + 2K_\perp)/3$$

Now since for any plane $\chi_\theta + \chi_{90+\theta} = \chi_{max} + \chi_{min}$. i.e. the sum of susceptibilities along the major and minor diameter of this section of the ellipsoid, hence instead of measuring χ_θ and $\chi_{90+\theta}$ we have determined $\chi_{max} + \chi_{min}$ by measuring the χ_{max} and the anisotropy $(\chi_{max} - \chi_{min})$ in the horizontal plane with c-axis vertical by the following elegant standard methods developed in our laboratory. A practically torsionless unspun silk fibre was used for suspension of the crystal in the desired orientation in a horizontal magnetic field with a vertical gradient from one arm of a jewel pivoted microbalance (Das, 1963) with electrodynamic conpensation device of the vertical magnetic pull on the crystal. The χ_{max} direction in the horizontal plane of the crystal automatically sets itself in the direction of the strong horizontal magnetic field and the value of χ_{max} is determined under this condition by measuring the vertical pull on the crystal. Since there is no appreciable horizontal gradient the effect of the anisotropy of shape of the crystal which moreover is chosen for uniform lateral development is negligible. Anisotropy with c-axis vertical was also determined using quartz-fibre suspension and measuring the maximum couple in a uniform field with the usual null deflection method (Krishnan and Banerjee, 1935; Dutta, 1954). The mean susceptibility was measured with a powdered sample using the same microbalance. Using equation (10) and α_3 and α'_3 equal to ·65236 and ·40182 respectively, ionic susceptibilities and anisotropy of $CuSO_4 . 5H_2O$ have been found out; the results are given in Table I.

TABLE I

$CuSO_4 \cdot 5H_2O$ — Temperature = 300°K

c axis vertical					
$\chi_{max} \times 10^6$	$(\chi_{max} - \chi_{min}) \times 10^6$	$\bar{\chi} \times 10^6$	$K_{\|} = 10^6$	$K_\perp = 10^6$	$(K_{\|} - K_\perp) \times 10^6$
1627	182	1524	1906	1335	573 (550)

value obtained by the earlier method is given within bracket (Krishnan and Mookherjee, 1936; 1938)

(b) *Application in the special case of orthorhombic crystals* :

The X-ray analysis of $NiSO_4$. $7H_2O$ (Beevers and Schwartz, 1935) shows that the crystal belongs to the orthorhombic class (space group D_2^4) with four approximately tetragonally distorted ions in the unit cell. In an ortho-rhombic crystal the direction cosines (α_3, β_3, γ_3) of the symmetry axis (T) of an ion with respect to a, b, and c respectively have the same magnitudes for each ion as required by the symmetry conditions, although there may be reversal of signs in some values. Since all that is necessary in the equations to be used is the square of the direction cosines, we quote below the magnitudes only :

	a	b	c
T	0.2840	0.8406	0.4695

Taking x, y and z axes to coincide with a, b and c axes of the crystal respectively the equation (2) becomes (with $K_1 = K_2 = K_\perp$, $K_3 = K_\parallel$ and $n = 4$)

$$\left.\begin{aligned}
&\text{(i) for } a\text{-axis vertical } (\xi = 1,\ \eta = \zeta = 0)\\
&\qquad \chi_{max}+\chi_{min} = K_\parallel(1-\alpha_3^2)+K_\perp(1+\alpha_3^2)\\
&\text{(ii) for } b\text{-axis vertical } (\eta = 1,\ \xi = \zeta = 0)\\
&\qquad \chi_{max}+\chi_{min} = K_\parallel(1-\beta_3^2)+K_\perp(1+\beta_3^2)\\
&\text{(iii) for } c\text{-axis vertical } (\zeta = 1,\ \xi = \eta = 0)\\
&\qquad \chi_{max}+\chi_{min} = K_\parallel(1-\gamma_3^2)+K_\perp(1+\gamma_3^2)
\end{aligned}\right\} \quad \ldots \quad (11)$$

Using these equations (11) and the expression (9) for mean susceptibility, ionic susceptibilities and anisotropy have been found out for different directions of suspension and the results are given in Table II. The experimental results of crystalline anisotropies and mean susceptibility have been taken from earlier measurements (Mookherjee, 1946;Jackson, 1925) and $\chi_{max}+\chi_{min}$ calculated from these values. In the calculation we have utilised the fact that in an ortho-rhombic crystal, the principal crystalline susceptibility axes coincides with the principal

TABLE II

$NiSO_4$, $7H_2O$ Temperature = 300°K

Orientation	$\chi \times 10^6$	$(\chi_{max}-\chi_{min}) \times 10^6$	$(\chi_{max}+\chi_{min}) \times 10^6$	$K_\perp \times 10^6$	$K_\parallel \times 10^6$	$(K_\perp - K_\parallel) \times 10^6$
a-axis vertical	4578.4	124.0 ($\chi_c-\chi_b$)	9091.0 ($\chi_c+\chi_b$)	4664.5	4406.2	258.7 {255.1}
b-axis vertical		33.5 ($\chi_a-\chi_c$)	9254.3 ($\chi_a+\chi_c$)	4665.4	4405.0	260.4 {239.7}
c-axis vertical		163.0 ($\chi_a-\chi_b$)	9124.8 ($\chi_a+\chi_b$)	4695.0	4345.0	249.9 {260.4}

The values within braces are obtained by earlier method (Lonsdale and Krishnan, 1936).

crystal axes and $\bar{\chi} = \frac{1}{3}(\chi_a+\chi_b+\chi_c)$. We could have as well directly measured χ_c and χ_a with the help of the micro-balance described earlier suspending the crystal vertically along a and b axes respectively.

In the above table measurements for different orientations are given for the purpose of comparison of the present method with the earlier one and the significance of tue differences in the values is discussed in the following section.

DISCUSSIONS

It is readily seen from Table I and II that the values of ionic anisotropy determined by the present method are in fairly good agreement with the earlier measurements. The difference in the case of $CuSO_4.5H_2O$ may be attributed to the approximation and trial and error solution of Krishnan and Mookerjee's method and small errors in the X-ray data. It is clear that the method presented in this paper is of the greatest convenience in the case of triclinic crystals where the ionic susceptibilities, which are the ultimate quantities of interest, can be directly arrived at without the difficult intermediate calculation of crystalline susceptibilities. It may be applied to other classes as well with great advantage. Even when the unit cell of the triclinic crystal contains one ion only or two inversionally equivalent ions in which case the crystalline and ionic values are identical, the method may be considered to be more convenient than solving for principal crystalline susceptibilities directly which involves greater number of measurements and laborious calculations, provided angular parameters are known precisely. In the case of orthorhombic crystals, ionic anisotropy can also be calculated following the method of Lonsdale and Krishnan (loc. cit.) in which case the expression comes in the form

$$K_\perp - K_\parallel = \frac{\chi_b-\chi_a}{\alpha_3^2-\beta_3^2} = \frac{\chi_c-\chi_a}{\alpha_3^2-\gamma_3^2} = \frac{\chi_c-\chi_b}{\beta_3^2-\gamma_3^2}$$

From the form of the above expression which contains a difference of the squares of two angular parameters in the denominator, it is evident that a small change in the X-ray angle will result in a large change in the ionic anisotropy calculated by the above method and thus the accuracy of the method is largely determined by the accuracy of the X-ray data, whereas, the determination of the ionic anisotropy in the present method is not so sensitive to small errors in X-ray data specially when the working plane is so chosen that angle involved is not near 45°.

The results of specific calculations by the two methods for three different directions of suspension, a, b and c axes of $NiSO_4$, $7H_2O$ given in the table II will clearly bring out the relative merit of our method of calculation. The variation from one axis to the other in the value of ($K_\perp - K_\parallel$) although percep-

tible is comparatively smaller in our method. The difference in the third value is evidently due to errors in the X-ray value of the angle γ_3.

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